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KURODA KOJI****(54) HARD CARBON AND ITS PRODUCTION****(57)Abstract:**

PURPOSE: To obtain hard carbon optimum for a part material required of high hardness, e.g., cutting tools, digging tools or a sliding part material, further having electroconductivity.

CONSTITUTION: This hard carbon is a mixture of an amorphous carbon and a diamond-resembled structure having $\geq 2000 \text{ kgf/mm}^2$ Vickers hardness and $1 \times 10^{-3} - 1 \times 10^{-1} \Omega \cdot \text{cm}$ electric resistance (at room temperature). This material is obtained by using a carbon cluster such as fullerenes as a raw material and using Al flux, as necessary, and using a belt cylinder-type high pressure machine or a piston cylinder-type high pressure machine at $\geq 2.0 \text{ GPa}$ pressure and at $600 - 900^\circ \text{C}$.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] If this invention relates to hard carbon and its manufacture method and it ****, it is related with the hard carbon and its manufacture method of the bulk further with [it is very hard and] conductivity which Vickers hardness (Hv) tells two or more [2000 kgf(s)/mm] to, and electrical resistivity tells 1×10^{-3} - 1×10^{-1} ohm-cm (room temperature). Especially the hard carbon concerning this invention is the the best for the various members as which hardness is required, for example, a cutting tool, the member for digging, and a sliding component.

[0002]

[Description of the Prior Art] Conventionally, well-known hard carbon could be manufactured by the laser ablation method besides [which decomposes and manufactures hydrocarbon system gas in plasma] a plasma CVD method, the ion plating method, the spatter, etc., and existed as a film which covers base materials, such as a super-high alloy and a ceramic. Since this hard carbon film has a high degree of hardness and it has abrasion resistance, it is widely used as surface-protection films, such as a cutting tool and a sliding component, (JP,61-30671,A, JP,4-354873,A, etc.).

[0003] Moreover, as a sliding component which needs conductivity, such as an electrical part, material with graphite structure like artificial-graphite material is used. This employs efficiently the outstanding self-lubricity and outstanding conductivity which are the property of graphite material.

[0004] On the other hand, carbon clusters, such as C60, come to be able to carry out extensive manufacture, and the attempt which manufactures the matter new as a raw material and compounds ***** is made in recent years. For example, [M. which Regueiro and others used C60 as the raw material, and has succeeded in composition of a cubic diamond polycrystal by the high pressure of 20 or more GPas in the shock high pressure process They are N.Regueiro and P.Monceau and J.L.Hodeau and Nature355,237(1992)].

[0005]

[Problem(s) to be Solved by the Invention] By the way, as mentioned above, since conventional hard carbon was able to be manufactured by the plasma CVD method etc., it only existed as a surface-protection film which covers the front face of various base materials. So, by accumulation of the internal stress accompanying film formation, if thickness becomes large, the problem which produces breakaway is held in the hard carbon film. Moreover, when elasticity material, such as stainless steel, was used as a base material, the size of a base material might change with film formation. Furthermore, the electrical resistivity of the conventional hard carbon film is in an almost electric insulating field called 1×10^5 - 1×10^{15} ohm-cm (room temperature), and was not suitable for the sliding component of which conductivity is required.

[0006] Then, this invention is new matter called the hard carbon of bulk, and a degree of hardness is very high and it aims at moreover offering hard carbon with conductivity, and its manufacture method.

[0007]

[Means for Solving the Problem] Amorphous carbon and the matter of diamond similar structure are intermingled, Vickers hardness (Hv) is two or more [2000 kgf(s)/mm], and the electrical resistivity of the hard carbon concerning this invention is the thing of 1×10^{-3} or 1×10^{-1} ohm-cm (room temperature).

[0008] Moreover, that Hv can generate the hard carbon of a high degree of hardness from 2 to the degree of hardness of a diamond 2000 kgf(s)/mm also found out this invention persons by using a carbon cluster as a raw material, and pressurizing and heating a raw material at 2.0 or more GPas of pressures, temperature 600, or 900 degrees C. Furthermore, that the hard carbon which has such a high degree of hardness is also generable found out by using the raw material which is aluminum 0.001 or 8 (mass ratio) to the carbon cluster 1, and pressurizing and heating a raw material at 2.0 or more GPas of pressures, temperature 660, or 900 degrees C.

[0009] Moreover, when manufacturing hard carbon, it is desirable to carry out using belt cylinder type high pressure installation or piston cylinder type high pressure installation.

[0010] Hereafter, the hard carbon concerning this invention is explained according to the example of the manufacture method.

[0011] the fullerene with which the carbon cluster which can be used as a raw material is represented by C60 -- it is expressed with the general molecular formula C_n like, and, as for the carbon atomic number n, high order fullerene, such as 70, 76, 78, 82, etc. besides 60, is mentioned If the structure is said in detail, C60 is a carbon cluster with a diameter of about 0.7nm which 60 carbon atoms present the shape of a football (Ih point group), and the regular pentagon has 12 pieces and structure to which the carbon atom existed [the right hexagon] in each vertex of 20 face pieces [32], for example. Such a carbon cluster is used for a

raw material, and this is pressurized and heated on condition that predetermined.

[0012] Moreover, when aluminum (aluminum) was mixed to the carbon cluster, the degree of hardness of the hard carbon obtained is high, and the bird clapper became clear by experiment of this invention persons. The melting point (660 degrees C) of aluminum is low, and in order that it may react with carbon and may generate an aluminium carbide (aluminum $4C_3$), it is considered to do the operation as a fusing agent so in the 660-900-degree C temperature field which is one of the manufacture conditions of this invention. Here, in using aluminum, as for aluminum, 0.001-8 are suitable with the mass ratio to the carbon cluster 1. It is because the degree of hardness of the hard carbon which will be obtained if a fusing agent operation cannot fully be done so but 8 is exceeded may fall less than by 0.001. In case it manufactures, since a carbon cluster is powder, aluminum also uses a powdered thing, these are mixed and, usually it fabricates in the shape of a pellet.

[0013] Such a carbon cluster is used as a raw material, and when using the pressure of 2.0 or more GPa and the temperature of 600-900 degrees C, or aluminum with aluminum added if needed, the temperature of 660-900 degrees C is presented, and the hard carbon concerning this invention is manufactured. Here, the reason for having chosen temperature conditions as 600-900 degrees C is explained. If it becomes 600 degrees C or more, it will begin to be decomposed, and if a carbon cluster amounts to 900 degrees C, it will be decomposed completely. In order to manufacture and compound the new matter, employing efficiently the unique property which a carbon cluster has, this temperature requirement is the optimal. Therefore, temperature conditions were set as the range of 600-900 degrees C, and when the flow and pressure requirement suitable for this temperature requirement was verified by experiment and it was the pressure of 2.0 or more GPa, it found out that the hard carbon concerning this invention could be manufactured. About the upper limit of a pressure, it usually carries out on balance with a manufacturing cost at 5 or less GPa. Moreover, when using aluminum, the melting point of aluminum is taken into consideration and it carries out in 660-900 degrees C.

[0014] In order to make it such a pressure and temperature conditions, belt cylinder type high pressure installation or piston cylinder type high pressure installation is usually used. The typical example of composition of these equipments was shown in drawing 4 - drawing 6. Drawing 4 is drawing in which the example of sample composition and drawing 5 showed the so-called flat belt type high pressure installation, and drawing 6 showed piston cylinder type high pressure installation typically, respectively as an example of belt cylinder type high pressure installation. It is more desirable to constitute a sample so that it may become the pressurization of 1 shaft orientations in which SP3 bond which constitutes the diamond similar structure field is easy to be formed, in order to obtain the hard carbon of a higher degree of hardness here, in case a pressure is applied. The example which made drawing 4 constitute a sample so that it may become the pressurization in 1 shaft orientations is shown.

[0015] In drawing 4, 1 is sample space, 2 is a specimen container, and it becomes a container for putting in aluminum added a raw material carbon cluster and if needed. If a specimen container 2 is made the product made from an alumina (aluminum $2O_3$), since preventing fixing with the hard carbon obtained will come out, it is an optimum. this specimen container 2 -- the upper and lower sides -- it has movable lid 2a, the pressure from pressure-medium 3a can be received, and the raw material in a specimen container 2 can be compressed. Usually, pressure-medium 3a uses the powder which consists of NaCl-ZrO₂. 4 is a graphite heater and can heat a raw material to desired temperature.

[0016] Drawing 5 shows typically a part of cross section of belt cylinder type high pressure installation. A sample can be pressurized by arranging the sample constituted like drawing 4 in the sample room 13, and generating a pressure between Anville (usually product made from a super-high alloy) 12, and a cylinder (usually product made from a super-high alloy) 11. A gasket 9 can usually consist of a PAIRO ferrite, and can close the generated pressure. The compressive gasket 10 is arranged on the outside of this gasket 9. Usually, using a laminating paper gasket, the compressive gasket 10 can deform in connection with the movement of Anville 11, and can produce a process required for pressurization. Current can be passed at the graphite heater 4 through the electrode 8 made from nickel from the energization ring 6.

[0017] Drawing 6 shows typically the cross section of piston cylinder type high pressure installation. The equipment shown in this drawing is based on Boyd-Englang type equipment. The developmental mechanics of the pressure by piston cylinder type high pressure installation makes the inside 31 of the wall of the tubed cylinder core 24, i.e., a sample room, generate a pressure by advance of a piston 26. A piston 26 is pushed up with the piston ram 30 through the piston cradle 27, and can make the sample room 31 generate a pressure with the equipment shown in this drawing. A back-up ring 25 is arranged at the nose of cam of the end plug 22 and a piston 26, and it prevents that a pressure medium overflows into the crevice between the cylinder cores 24. The piston shrinkage ring 28 controls the lateral pressure to a piston 26 by the press thrust.

[0018] Generally, belt cylinder type high pressure installation has few component parts, and can be produced easily. On the other hand, piston cylinder type high pressure installation is good, and the controllability and repeatability of a pressure are stabilized and can produce it. In this invention, 2.0 or more GPa of pressures can be pressurized, and which equipment may be used that what is necessary is just to use the equipment which can carry out a temperature up to the temperature of 600-900 degrees C.

[0019] Such equipment etc. is used, the pressure of 2.0 or more GPa, the temperature of 600-900 degrees C, or 660-900 degrees C are presented with a raw material, and the hard carbon concerning this invention is manufactured. The hard carbon obtained makes amorphous carbon a subject, and has the property peculiar to hard carbon in which a degree of hardness is very high. Moreover, only with amorphous carbon, since it does not become a high degree of hardness called 2 or more [2000 kgf(s)/mm] and 2 or more [further 4000 kgf(s)/mm], it is thought that the matter with diamond similar structure is intermingled in this. moreover, it should hear that the matter of diamond similar structure is intermingled also from the result of the Raman spectrum mentioned later or the temperature dependence of thermal conductivity -- ** And it can be surmised that the field of diamond more similar [than the result of an X-ray diffraction method] structure since the peak of the matter cannot be observed is 2nm or less in size. The matter of this diamond similar structure originates in having used the carbon cluster for the raw material, and the

carbon cluster which has the property to be easy to join together SP3 can be considered that the part changed with pressurization and temperature ups to diamond similar structure. It is thought that the cage of a carbon cluster was destroyed completely and amorphous carbon changed to amorphous carbon on the other hand. Moreover, it can be surmised that SP2 field which has conductivity is in a percolation state since the obtained hard carbon has conductivity.

[0020]

[Example] Hereafter, based on an example, the hard carbon concerning this invention and its manufacture method are explained.

[0021] It preformed on the pellet with a diameter [of 4mm] x thickness of 3mm by having used the example 1 C60 as the raw material, and the sample was constituted like drawing 4 . And it pressurized to the predetermined pressure using the piston cylinder type high pressure installation shown in the belt cylinder type high pressure installation or drawing 6 shown in drawing 5 , and temperature was lowered and the pressure was released, after carrying out the temperature up and holding as it is to predetermined temperature for 2 hours. The pressure performed temperature from 2.0 to 4.0GPa(s) on condition that the various kinds to 600 to 900 degrees C. All the obtained samples were presenting the shape of a pellet which preformed mostly.

[0022] An example 2C60 and aluminum powder were mixed at a predetermined rate, and it manufactured by the same method as an example 1 except having carried out the temperature up from temperature 660 to 900 degrees C. The mixed rate of aluminum powder was performed in the ranges from 0.001 to 8 to C601 by the weight ratio. All the obtained samples were presenting the shape of a pellet which preformed mostly.

[0023] all the samples obtained in the examples 1 and 2 -- appearance observation, bulk density, a BIKASU degree of hardness, an X diffraction, and Raman -- a spectrum, electrical resistivity, and thermal conductivity were measured Hereafter, the result is described according to a parameter.

[0024] <Appearance observation> Although the obtained sample was black as a whole, when the direction of a sample was finely guessed with the optical microscope, there were a bright portion and a dark portion. In addition, both cope with a Raman spectrum which is different so that it may mention later. Moreover, when the front face was observed with the scanning electron microscope and the optical microscope, there is also no generating of pore or a void and it turns out that it is quite homogeneous. Furthermore, the typical photograph which observed the sample front face with the atomic force microscope (AFM) is shown in drawing 7 . This view shows that the sample is constituted with the lump which presented the spherical mostly. Moreover, it is thought that about 100 raw material C60 molecules gathered, and it constituted this lump by pressurization and the temperature up since the lump's average size was about 100nm.

[0025] The bulk density of a <bulk density measurement> sample was 1.8 - 2.0 g/cm³. Although this value differs from the start raw material C60 (bulk density 1.7 g/cm³) or a diamond (bulk density 3.5 g/cm³) clearly, it is within the limits of the bulk density 1.8 of well-known amorphous carbon - 2.1 g/cm³ conventionally.

[0026] The <Vickers determination of hardness> When all the samples were very hard and the board of glass or sapphire was scratched, they were able to attach the blemish to those front faces easily. Moreover, when the degree of hardness of a sample was measured with the Vickers hardness meter (the NIKON CORP. make, load 1kgf) by the diamond indenter, the degree of hardness was increasing like what is two or more [2000 kgf(s)/mm] altogether, and made [many] the amount of aluminum powder. aluminum powder of the samples from 5 to 8 was [as opposed to / C601 / especially] two or more / 4000 kgf(s)/mm /. It turns out that it is clearly large and this value is closer to the value of a diamond thin film than 2 the 800 to 1200 kgf/mm degree of hardness of a glassy carbon.

[0027] The X-ray (copper K alpha rays, wavelength of 0.154nm) was irradiated on the <measurement by X-ray diffraction method> sample front face, and the X-ray diffractometer (the Rigaku make, "RINT1000") investigated the structure of a sample. The example of representation of the diffraction pattern is shown in drawing 1 . As shown in this drawing, the latus diffuse peak of width of face can be observed in the position whose angle-of-diffraction 2theta is about 26 degrees, about 43 degrees, and about 80 degrees, and these peak positions correspond to about 0.347nm, about 0.209nm, and about 0.119nm in d space, respectively. However, the peak resulting from C60 or a diamond has not been observed. As for the obtained sample, it turns out that it is the amorphous carbon structure where the microcrystal is seldom developed from the size of this peak width to graphite structure, and the half peak width (full width at half maximum) showed that the size of the microcrystal was 5-50nm.

[0028] The <measurement by Raman spectroscopy> sample front face was ground, and the micro Raman spectroscopy estimated the sample (light source : helium-Ne laser, wavelength : 632.8nm, an output : 22.5mW, spot size : 2 micrometers). As for the Raman spectrum, two kinds of things (it is described as a and b) were obtained from the same sample. The typical spectrum is combined with drawing 2 , and is shown. a in this drawing and b are the spectrums from the dark portion a in a sample front face, and the bright portion b, as mentioned above. As shown in a, as for all samples, the latus peak of width of face existed in the position of the 1590**10cm⁻¹ neighborhood and the 1320**10cm⁻¹ neighborhood. the size of this peak width -- various kinds -- since it sees also to well-known amorphous carbon mostly, it can be surmised that the obtained sample is also amorphous It is thought that it is based on SP2 combination since the peak of this 1590cm⁻¹ neighborhood is close to 1581cm⁻¹ (SP2 combination) corresponding to the peak of crystalline high graphite. Moreover, the peak of the 1320cm⁻¹ neighborhood reflected the irregularity of a graphite grid, namely, since it is close to 1355cm⁻¹ corresponding to the peak of bad crystalline carbon, as for a sample, crystallization is considered to be seldom developed. Moreover, although this peak can ask 1332cm⁻¹ corresponding to a diamond (SP3 combination) about existence of the matter of near and diamond similar structure, the width of face of a peak completely differs and the direction of a sample is quite large. Moreover, all of the relative intensity ratio of the peak of this 1320cm⁻¹ neighborhood and the peak of the 1590cm⁻¹ neighborhood and the so-called R value were within the limits of 0.5-1.2. On the other hand, the peak which clarified in this way was not looked at by b which is a spectrum from portion with an another sample front face, but has observed to it only the peak of latus width of face called 1250-1600cm⁻¹. This shows clearly that a

sample is the amorphous matter.

[0029] The electrical resistivity of a <measurement of electrical resistivity> sample was measured by 4 terminal method. The electrical resistivity in a room temperature of all the samples was within the limits of 1×10^{-3} - 1×10^{-1} ohm-cm. Moreover, as for every sample, electrical resistivity had the property like a semiconductor to become high as temperature became low. Although the value of electrical resistivity is not so much different from the typical value of a well-known glassy carbon conventionally, temperature dependence completely differs. As an example of representation which shows the temperature dependence of electrical resistivity, three kinds of samples, I, RO, and HA, are shown in drawing 3. The sample which I used only C60 as the raw material, and was manufactured at pressure 2.6GPa and the temperature of 700 degrees C here, As for RO, aluminum mixes aluminum powder at a rate of 3 (mass ratio) to C60 in the raw material of C60. The sample manufactured at pressure 2.6GPa and the temperature of 700 degrees C and HA are the samples which aluminum mixed aluminum powder at a rate of 6 (mass ratio) to C60 in the raw material of C60, and were manufactured at pressure 2.6GPa and the temperature of 700 degrees C. Every sample of the rate of change of the electrical resistivity from a room temperature to 4.2K was 5 - 30% of within the limits. Moreover, this sample has the feature also in having almost linear temperature dependence.

[0030] The thermal conductivity of a <measurement of thermal conductivity> sample was measured by the temperature requirement of 30-350K. The thermal conductivity of a sample was 5 - 20W/(m-K) at the room temperature, and the value became small-like proportionally mostly as temperature became low. Especially, it was decreasing almost linearly, and when a room temperature to about 80K became below this temperature, it changed so that it might separate from this straight line. Such temperature dependence resembles the temperature dependence of diamond similar carbon.

[0031]

[Effect of the Invention] Unlike the film of conventional hard carbon, the hard carbon concerning this invention is a completely new body called the hard carbon of bulk, and Vickers hardness can apply it now to the use of the various fields as which business of this is carried out and high degrees of hardness, such as a cutting tool and a sliding component, are required since it has the stiff property very much of 2 or more [2000 kgf(s)/mm] and 2 or more [further 4000 kgf(s)/mm]. Furthermore, since it has the high degree of hardness upwards and electrical resistivity also has the property of a low, the hard carbon concerning this invention can be used effective in the field of the sliding component of which conductivity is required, or semiconductor electronics.

[0032] Moreover, by this invention, the hard carbon of a high degree of hardness with which Vickers hardness closes in upon a diamond called 2 or more [2000 kgf(s)/mm] and 2 or more [further 4000 kgf(s)/mm] can be compounded now on condition that low voltage and low temperature compared with composition of a diamond called the pressure of 2.0 or more GPas, and the temperature of 600-900 degrees C, it can be cheap and the hard matter can be easily manufactured now.

[Translation done.]